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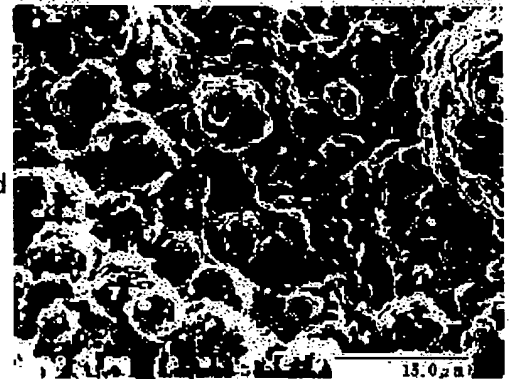
(72)Inventor : MATSUMOTO TOMOO

(54) PRODUCTION METHOD FOR CALCIUM PHOSPHATE-BASED POROUS CERAMIC SINTERED COMPACT AND CALCIUM PHOSPHATE-BASED POROUS CERAMIC SINTERED COMPACT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a production method for a calcium phosphate-based porous ceramic sintered compact having moderate porosity and high strength.

SOLUTION: This method for producing a calcium phosphate-based porous ceramic sintered compact having 5 to 50% of porosity by utilizing the gelation of a water soluble polymer comprises (1) making a slurry containing a calcined calcium phosphate-based ceramic powder and a water soluble polymer compound, (2) pulverizing and dispersing the ceramic powder in the slurry by agitating it, (3) performing a gelation, and (4) sintering after drying.



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(71)出願人 000000527

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ペンタックス株式会社

東京都板橋区前野町 2丁目36番 9号

(72)発明者 松本 智勇

東京都板橋区前野町 2丁目36番 9号 旭光

学工業株式会社内

(74)代理人 100080012

弁理士 高石 橋馬

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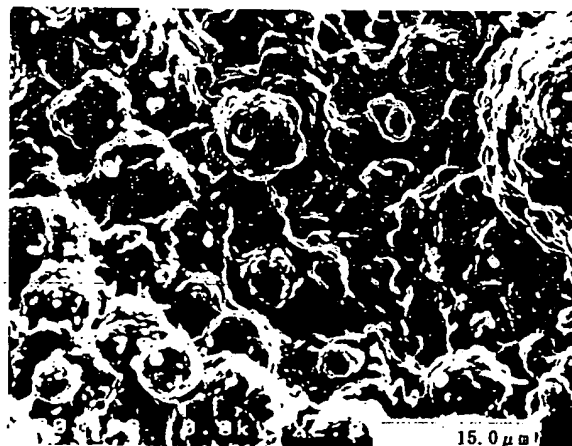
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(54)【発明の名称】 多孔質リン酸カルシウム系セラミックス焼結体の製造方法及び多孔質リン酸カルシウム系セラミックス焼結体

(57)【要約】

【課題】 適度な気孔率と高強度を有する多孔質リン酸カルシウム系セラミックス焼結体の製造方法を提供する。

【解決手段】 水溶性高分子のゲル化を利用して気孔率5~50%を有する多孔質リン酸カルシウム系セラミックス焼結体を製造する方法において、(1)仮焼処理を施したリン酸カルシウム系セラミックス粉体と水溶性高分子化合物とを含有するスラリーを作製し、(2)スラリーを強く攪拌することによりリン酸カルシウム系セラミックス粉体を粉砕・分散し、(3)ゲル化させ、(4)乾燥後に焼結する方法。



【特許請求の範囲】

【請求項 1】 水溶性高分子のゲル化を利用して気孔率が 5～50% の多孔質リン酸カルシウム系セラミックス焼結体を製造する方法において、(1) 仮焼処理を施したリン酸カルシウム系セラミックス粉体と水溶性高分子化合物とを含有するスラリーを作製し、(2) 前記スラリーを強く攪拌することにより前記リン酸カルシウム系セラミックス粉体を粉砕・分散し、(3) ゲル化させ、(4) 乾燥後に焼結することを特徴とする多孔質リン酸カルシウム系セラミックス焼結体の製造方法。

【請求項 2】 請求項 1 に記載の多孔質リン酸カルシウム系セラミックス焼結体の製造方法において、前記リン酸カルシウム系セラミックス粉体は平均長軸長が 100 nm 以下のリン酸カルシウム系セラミックスの一次粒子からなる平均粒径 5～20 μm の球状の二次粒子であることを特徴とする多孔質リン酸カルシウム系セラミックス焼結体の製造方法。

【請求項 3】 請求項 1 又は 2 に記載の多孔質リン酸カルシウム系セラミックス焼結体の製造方法において、前記リン酸カルシウム系セラミックス粉体の Ca/P の重量比は 1.5～1.7 であることを特徴とする多孔質リン酸カルシウム系セラミックス焼結体の製造方法。

【請求項 4】 請求項 1～3 のいずれかに記載の多孔質リン酸カルシウム系セラミックス焼結体の製造方法において、前記仮焼処理を 700～850℃ で行うことを特徴とする多孔質リン酸カルシウム系セラミックス焼結体の製造方法。

【請求項 5】 請求項 1～4 のいずれかに記載の多孔質リン酸カルシウム系セラミックス焼結体の製造方法において、前記水溶性高分子化合物はセルロース誘導体であることを特徴とする多孔質リン酸カルシウム系セラミックス焼結体の製造方法。

【請求項 6】 請求項 1～5 のいずれかに記載の多孔質リン酸カルシウム系セラミックス焼結体の製造方法において、前記スラリーの攪拌を 50 W/L 以上の攪拌力により行うことを特徴とする多孔質リン酸カルシウム系セラミックス焼結体の製造方法。

【請求項 7】 請求項 1～6 のいずれかに記載の多孔質リン酸カルシウム系セラミックス焼結体の製造方法において、前記スラリーの攪拌粉砕・分散処理を 1～60 分間行うことを特徴とする多孔質リン酸カルシウム系セラミックス焼結体の製造方法。

【請求項 8】 請求項 1～7 のいずれかに記載の多孔質リン酸カルシウム系セラミックス焼結体の製造方法において、前記リン酸カルシウム系セラミックス粉体 100 重量部に対して、前記水溶性高分子化合物 1～10 重量部を配合することを特徴とする多孔質リン酸カルシウム系セラミックス焼結体の製造方法。

【請求項 9】 請求項 1～8 のいずれかに記載の多孔質リン酸カルシウム系セラミックス焼結体の製造方法にお

いて、前記スラリー中における前記リン酸カルシウム系セラミックス粉体+前記水溶性高分子化合物の合計濃度は 20～50 重量%であることを特徴とする多孔質リン酸カルシウム系セラミックス焼結体の製造方法。

【請求項 10】 請求項 1～9 のいずれかに記載の多孔質リン酸カルシウム系セラミックス焼結体の製造方法において、前記リン酸カルシウム系セラミックス粉体がハイドロキシアパタイト粉体であることを特徴とする多孔質リン酸カルシウム系セラミックス焼結体の製造方法。

10 【請求項 11】 請求項 1～10 のいずれかに記載の多孔質リン酸カルシウム系セラミックス焼結体の製造方法により得られる多孔質リン酸カルシウム系セラミックス焼結体。

【請求項 12】 請求項 11 に記載の多孔質リン酸カルシウム系セラミックス焼結体において、15 MPa 以上の 3 点曲げ強度を有することを特徴とする多孔質リン酸カルシウム系セラミックス焼結体。

【発明の詳細な説明】

【0001】

20 【発明の属する技術分野】本発明は、細胞及び生体組織の培養に用いる担体や骨補填用等に好適な生体親和性を有する人工生体材料のみならず、液体クロマトグラフィー用充填剤、触媒担体、各種の電気・電子材料、原子炉材料、セラミック発熱体等にも有用な多孔質リン酸カルシウム系セラミックス焼結体を製造する方法及びその製造方法により得られる多孔質リン酸カルシウム系セラミックス焼結体に関し、特に高強度を有する多孔質リン酸カルシウム系セラミックス焼結体を製造する方法及びその製造方法により得られる多孔質リン酸カルシウム系セラミックス焼結体に関する。

【0002】

30 【従来の技術及び発明が解決しようとする課題】セラミックスは近年急速に技術革新が進み、耐熱性、機械的強度、絶縁性、強誘電性、圧電性、半導電性、磁性等を応用した各種の耐熱材、構造材及び機能材が開発されている。なかでもリン酸カルシウム系セラミックス（例えばハイドロキシアパタイト）は歯や骨の無機成分と構造が似ているために、優れた生体適合性を有し、人工歯根や骨補填材、歯科用セメント等の生体材料として用いられている。

40 【0003】生体親和性の観点から、リン酸カルシウム系セラミックスは多孔質なほど、すなわち気孔率が高いほど良い。このため従来から多孔質リン酸カルシウム系セラミックスを製造する方法として、水溶性高分子ゲル化法が提案されている。水溶性高分子ゲル化法は、セラミックスと水溶性高分子化合物とのスラリーを攪拌することにより起泡させ、起泡したスラリーを加熱することによりゲル化させ、気泡を保持した状態で乾燥する方法である（特許 3058174 号）。特許 3058174 号の方法により得られた多孔質セラミックスは、気泡に由来する孔径

20 ~ 2000 μm の球形のマクロポアと、セラミックス原料一次粒子の凝集体からなる球状二次粒子粉体の間隙によって形成される3次元連通孔とを有する。

【0004】しかしながら、このような水溶性高分子ゲル化法により得られる多孔質リン酸カルシウム系セラミックスはマトリックス部分の焼結性が弱く、高い機械的強度を得るのが困難であり、曲げ強度等の機械的強度を改善する必要があった。

【0005】従って本発明の目的は、適度な気孔率と高強度を有する多孔質リン酸カルシウム系セラミックス焼結体の製造方法を提供することである。

【0006】

【課題を解決するための手段】上記課題に鑑み鋭意研究の結果、本発明者らは、仮焼処理を施したリン酸カルシウム系セラミックス粉体と水溶性高分子化合物とを含有するスラリーを強く攪拌することにより、適度な気孔率かつ高強度を有する多孔質リン酸カルシウム系セラミックス焼結体を得られることを発見し、本発明を完成した。

【0007】すなわち、水溶性高分子のゲル化を利用して気孔率5 ~ 50 %を有する多孔質リン酸カルシウム系セラミックス焼結体を製造する本発明の方法は、(1) 仮焼処理を施したリン酸カルシウム系セラミックス粉体と水溶性高分子化合物とを含有するスラリーを作製し、(2) スラリーを強く攪拌することによりリン酸カルシウム系セラミックス粉体を粉砕・分散し、(3) ゲル化させ、(4) 乾燥後に焼結することを特徴とする。

【0008】リン酸カルシウム系セラミックス粉体は、平均長軸長（長軸方向の平均長さ）が100 nm以下のリン酸カルシウム系セラミックスの一次粒子からなる平均粒径が5 ~ 20 μm の球状の二次粒子からなるのが好ましい。二次粒子の平均粒径を5 ~ 20 μm とし、かつその形状を球状とすることにより、最終的な多孔質リン酸カルシウム系セラミックス焼結体となった時に梁となるマトリックス部分の太い焼結体を得られ、強度が向上する上、スラリーの攪拌性及びゲルの乾燥体であるグリーンブロックの成形性が向上する。リン酸カルシウム系セラミックス粉体のCa/Pの重量比は1.5 ~ 1.7 であるのが好ましい。

【0009】仮焼処理は700 ~ 850 $^{\circ}\text{C}$ の温度で行うのが好ましい。700 ~ 850 $^{\circ}\text{C}$ で行うことにより、焼結による粒成長を伴わずにリン酸カルシウム系セラミックス粉体の強度を向上させることができる。

【0010】水溶性高分子化合物はメチルセルロース、カルボキシメチルセルロース等のセルロース誘導体であるのが好ましい。スラリーの組成は、リン酸カルシウム系セラミックス粉体100重量部に対して、水溶性高分子化合物が1 ~ 10 重量部であるのが好ましい。これによりゲル化が容易になり、かつスラリー粘度が適度になるので二次粒子の粉砕が容易になる。またスラリー中にお

けるリン酸カルシウム系セラミックス粉体+水溶性高分子化合物の合計濃度は20 ~ 50重量%であるのが好ましい。これによりゲル化後の乾燥が容易になり、かつスラリー粘度が適度になるので二次粒子の粉砕が容易になる。

【0011】スラリーの攪拌粉砕・分散処理は50 W/L以上の攪拌力により行うのが好ましく、1 ~ 60 分間行うのが好ましい。

【0012】このような特徴を有する本発明の多孔質リン酸カルシウム系セラミックス焼結体の製造方法は、特に多孔質ハイドロキシアパタイト焼結体を製造する場合に好ましい。

【0013】本発明の製造方法により得られる気孔率が5 ~ 50 %の多孔質リン酸カルシウム系セラミックス焼結体は、マトリックス部分が太く且つその焼結性が強いいため、優れた機械的強度すなわち15 MPa以上の3点曲げ強度を有する。

【0014】

【発明の実施の形態】本発明の製造方法及びそれにより得られる多孔質リン酸カルシウム系セラミックス焼結体について、以下詳細に説明する。

【0015】[1] 製造方法

本発明に用いるリン酸カルシウム系セラミックスとしては、特に制限はないが、Ca/Pの重量比が1.5 ~ 1.7 のものが好ましく、例えばハイドロキシアパタイト、リン酸三カルシウム及びこれらの混合物が挙げられる。Ca/Pの重量比が1.7 超であると焼結後に酸化カルシウム(CaO)との混在相となるため好ましくない。逆に重量比が1.5より低くなるとリン酸カルシウム自体の分解が起こり易くなる。本発明の製造方法を適用する多孔質リン酸カルシウム系セラミックス焼結体の好ましい例は多孔質ハイドロキシアパタイト焼結体 $[\text{Ca}_{10}(\text{PO}_4)_6 \cdot (0.5\text{H}_2\text{O})_2]$ である。以下本発明の製造方法を多孔質ハイドロキシアパタイト焼結体を製造する場合を例にとりて詳細に説明するが、本発明は他のリン酸カルシウム系セラミックス焼結体にも適用することができる。

【0016】(1) スラリーの調製

ハイドロキシアパタイト粉体及び水溶性高分子化合物を含有するスラリーを調製する。

(a) ハイドロキシアパタイト粉体の調製

ハイドロキシアパタイト粉体は仮焼したものである必要がある。仮焼処理を施すことによりハイドロキシアパタイト粉体の強度が増加し、後述の粉砕時に過度の粉砕が行われず、粉砕度の制御が容易になるとともに、強い攪拌に耐える粉体強度が得られる。ハイドロキシアパタイト粉体は、平均長軸長が100 nm以下の一次粒子からなる平均粒径5 ~ 20 μm の球状の二次粒子からなるのが好ましい。一次粒子の平均長軸長が100 nmを超えると、一次粒子を造粒して二次粒子にした時にその結晶粒が粗大になり過ぎ、二次粒子の平均粒径が5 ~ 20 μm になり

難いのに加え、焼結も困難になる。一次粒子の平均長軸長は5～80 nmであるのが好ましい。二次粒子は一次粒子を造粒して顆粒状にする。ハイドロキシアパタイトの一次粒子を顆粒化するには、スプレードライ法等の公知の造粒法を利用することができる。二次粒子の平均粒径を5～20 μmとし、かつその形状を球状とすることにより、最終的な多孔質ハイドロキシアパタイト焼結体となった時に梁となるマトリックス部分の太い焼結体を得られ、強度が向上する上、スラリーの攪拌性及びゲルの乾燥体であるグリーンブロックの成形性が向上する。

【0017】仮焼処理工程では二次粒子に熱処理を施すが、700～850℃の温度で処理するのが好ましく、その処理時間は4～10時間であるのが好ましい。仮焼温度が700℃未満であるとハイドロキシアパタイト粉体の強度の十分な向上は達成できず、850℃超であると焼結が始まるので粒成長が起こる。より好ましい仮焼温度は700～750℃である。仮焼時間が4時間未満であると、成形性及びハンドリング性が実質的に向上しない。また10時間を超えると焼結反応が進行してしまい、成形後の焼結が不十分になる。なお仮焼は大気中で行うことができるが、酸化を防止する目的で不活性ガス中で行ってもよい。

【0018】(b) 水溶性高分子化合物

本発明に使用し得る水溶性高分子化合物は、その水溶液又は水分散液に対して加熱等の手段を施すことによりゲル化するものである。水溶液又は水分散液は、水溶液、コロイド溶液、エマルジョン及び懸濁液のいずれも包括する。このような水溶性高分子化合物として、例えばメチルセルロース、カルボキシメチルセルロース等のセルロース誘導体、カドラン等の多糖類、ポリビニルアルコール、ポリアクリル酸、ポリアクリルアミド、ポリビニルピロリドン等の合成重合体等が挙げられ、中でもメチルセルロースが好ましい。またポリビニルアルコールの場合、硼酸あるいは硼砂を添加することによりゲル化させることができる。

【0019】(c) 配合比及び濃度

スラリー中において、ハイドロキシアパタイト粉体を10重量部として、水溶性高分子化合物を1～10重量部にするのが好ましい。水溶性高分子化合物の添加量が1重量部未満であるとゲル化が困難であり、また10重量部超であるとスラリーの粘度が高くなり過ぎるため二次粒子の粉砕が困難になる。水溶性高分子化合物のより好ましい添加量は1～5重量部である。

【0020】スラリー中におけるハイドロキシアパタイト粉体+水溶性高分子化合物の合計濃度は20～50重量%であるのが好ましい。これらの成分の合計濃度が20重量%未満であるとゲル化後の乾燥に時間がかかり過ぎ、また乾燥後にゲルがつぶれて多孔質形状を維持できない。一方合計濃度が50重量%超であるとスラリーの粘度が高くなり過ぎるため、二次粒子の攪拌粉砕が困難

である。より好ましい合計濃度は25～40重量%である。

【0021】(2) 粉砕・分散

上記組成のスラリーを強く攪拌すると、仮焼した二次粒子すなわちハイドロキシアパタイト粉体を表面から粉砕することができる。粉砕により粒子の球状性が向上し、梁となるマトリックス部分の太い焼結体を得られ、その結果焼結体の強度を向上させることができる。また粉砕によって生じた微粉が二次粒子同士の結合剤となるため、焼結体の強度向上に寄与する。粉砕は、二次粒子の平均粒径が5～20 μmの範囲内に収まる程度に行うのが好ましい。これにより5～50%の適度な気孔率、高強度及び5～1500 μmの平均気孔径を有する焼結体を得ることができる。上記範囲の気孔率及び平均気孔径を有することにより、焼結体を人工生体材料として用いた場合に細胞の生着や各種生体組織の吸着が有利になる。二次粒子の平均粒径が5 μm未満であるとハンドリング性が向上しない上、粒子間隙が狭くなり、粒子の密度が上がり過ぎて5～50%の気孔率を得られない。また20 μmを超えると粒子同士の単位表面積当たりの接触範囲が減少し、互いの粒子同士の結合力が低下し、強度の点から骨補填材としての使用に耐え難くなる。

【0022】攪拌力は50 W/L以上であるのが好ましい。攪拌条件を50 W/L以上とすることにより、二次粒子を効率的に粉砕することができる。攪拌力が50 W/L未満であると粉砕が不十分であり、高い強度を有する多孔質ハイドロキシアパタイトが得られない。なお攪拌力は、[攪拌機の最大出力(W)/水溶液の量(L)]×(実際の回転数/最大回転数)により求まる。攪拌機の出力はスラリーの粘度が高くなる場合は、回転数を保つために見かけ上増大する。本発明の場合、スラリー中におけるハイドロキシアパタイト粉体+水溶性高分子化合物の合計濃度は20～50重量%であるためスラリー粘度は仕込み時の粘度から実質的に変化しない。従って、粘度の影響は実質的に無視できる。

【0023】このような攪拌力が得られる装置としてインペラー式ホモジナイザーが挙げられる。また攪拌羽根をディスク状にするとともに、ディスクの外周に鋸刃上の凹凸を設け、さらに攪拌容器の内壁に邪魔板を設けた構造の攪拌装置を使用するのが好ましい。このような構造を有するインペラー式ホモジナイザーは、例えばエスエムテール(株)製のPH91、PA92、HF93、FH94P、PD96、HM10等である。

【0024】攪拌時間は攪拌力に依存するが、一般的には1～60分間程度が好ましい。適度な気孔率の焼結体を得るには攪拌時に気泡を含ませるのが好ましく、気泡を微細かつ均一化させるとともに安定化させるために、比較的低温で攪拌を行うのが好ましい。具体的には約0～25℃、特に5～20℃の液温で行うのが好ましい。また攪拌中のスラリーに空気、窒素、アルゴン等の不活

性ガスを注入することにより気孔率のより高い焼結体を得ることができる。

【0025】粉砕・分散したスラリーは、内壁に可撓性耐水性膜を張った型に注型するのが好ましい。これにより乾燥時のセラミックスの収縮に伴って膜が型から剥離するので、型と接する面でのセラミックスの崩れや内部での割れが起こらず、優れた乾燥体を得られる。

【0026】(3) 真空脱泡

より緻密度の高い焼結体を得るためには、真空脱泡を行うのが好ましい。例えば上記の型に注型した後、真空オーブン等に入れて脱泡する。真空脱泡の条件が厳し過ぎると焼結体の気孔率が低くなるので好ましくない。一般的にはスラリーを40℃において0.1～1.0 torrで60～180分間脱泡すれば、緻密度と気孔率のバランスに優れた焼結体を得られる。

【0027】(4) ゲル化

攪拌により十分に粉砕・分散したスラリーを80℃以上100℃未満に加熱すると、メチルセルロース等の水溶性高分子化合物の作用によりゲル化する。加熱温度が80℃未満であるとゲル化が不十分であり、また100℃以上であると水分が沸騰し、ゲル構造が破壊される。

【0028】(5) 乾燥

ゲルの乾燥は、水分が沸騰しない程度の高温（例えば80℃以上～100℃未満）に保持することにより行うのが好ましい。ゲルは乾燥によりほぼ等方的に収縮するとともに、気泡に変化は起こらないため、割れ等を生ずることなく、微細かつ均一な球状のマクロポアを有する強度の高い乾燥体（グリーンブロック）となる。ほぼ水分がなくなれば100℃以上にしても良い。

【0029】(6) 加工

グリーンブロックに含有される水溶性高分子化合物はバインダーとして作用するので、ハンドリングできる機械的強度を有する。従ってグリーンブロックに対して仮焼成を行うことなく、乾燥体のまま切削加工することができる。

【0030】(7) 脱脂

所定の形状に加工したグリーンブロックから水溶性高分子化合物を除去するため、必要に応じて脱脂処理を行う。脱脂処理は300～900℃に加熱することにより行うことができる。

【0031】(8) 焼結

グリーンブロックを1000～1250℃で2～10時間大気中で焼結する。焼結温度が1000℃未満であると、十分な強度を有する多孔質ハイドロキシアパタイト焼結体を得られず、また1250℃超であるとハイドロキシアパタイトは磷酸三カルシウムと酸化カルシウムに分解してしまう。焼結時間は焼結温度に応じて適宜設定すれば良い。なお脱脂工程を省略する場合には、焼結温度に達するまで徐々に昇温することにより脱脂を兼ねることができ。例えば室温から約10～100℃/時の昇温速度で約

600℃まで昇温し、次に約50～200℃/時の昇温速度で焼結温度まで昇温し、この温度で保持するのが好ましい。焼結完了後は徐冷する。

【0032】[2] 多孔質リン酸カルシウム系セラミックス焼結体

本発明の製造方法により得られる多孔質ハイドロキシアパタイト焼結体を始めとする多孔質リン酸カルシウム系セラミックス焼結体は、適度な気孔率と高い曲げ強度を有することを特徴とする。(1) 気孔率本発明の多孔質リン酸カルシウム系セラミックス焼結体は5～50%の気孔率を有する。5%未満では生体親和性が十分でなく、50%超だと機械的強度が不十分なために加工性やハンドリング性に劣る。

【0033】(2) 曲げ強度

一般的に曲げ強度を始めとする機械的強度は気孔率が高くなるに従って低下するが、本発明の多孔質リン酸カルシウム系セラミックス焼結体はマトリックス部分が太く且つその焼結性が強いので、気孔率50%においても15MPa以上の3点曲げ強度を有する。このため加工性やハンドリング性に優れている。3点曲げ強度はJIS R1601に従って測定することができる。

【0034】(3) 平均気孔径

多孔質リン酸カルシウム系セラミックス焼結体の平均気孔径は5～1500μmであるのが好ましい。5μm未満だと細胞又は血管の侵入形成が困難となり、また1500μm超では安定した機械的強度を得るのが困難となるため、製品ロット毎に加工性やハンドリング性の変動幅が大きくなり過ぎる。多孔質リン酸カルシウム系セラミックス焼結体中の気孔径は均一であるのが好ましいので、大部分（80%以上）の気孔が50～500μmの範囲内の径であるのが好ましい。

【0035】

【実施例】本発明を以下の実施例によりさらに詳細に説明するが、本発明はこれらに限定されるものではない。

【0036】実施例1

細長い形状の一次粒子（平均径：長径78nm、短径23nm）からなるハイドロキシアパタイトの球状粉体（平均粒径：10μm）160gを700℃で大気中において4時間仮焼した。

【0037】得られた仮焼粉体（平均粒径：10μm、カルシウム／リン比 1.67）150gと、メチルセルロース（和光純薬工業（株）製、2重量%水溶液として20℃で測定した粘度：4000cps）の1重量%水溶液340gとを配合した。得られたスラリーをホモジナイザー（エスエムテ（株）製、PA92）に投入した。スラリー温度を8℃に保ちながら、スラリーを50W/Lの攪拌力（攪拌時の実際の出力、5500rpm）で15分間強く攪拌し、分散させるとともに仮焼粉体を粉砕した。

【0038】得られた気泡含有スラリーを型に注入し、83℃で2時間加熱し、ゲル化させた。得られたゲルを

83℃に保持することにより完全に乾燥し、グリーンブロックを得た。

【0039】グリーンブロックを12.0×22.0×7.0 mmの形状に加工した後、大気中で室温から50℃/時の昇温速度で600℃まで昇温し、次に100℃/時の昇温速度で1200℃まで昇温し、この温度で4時間焼成した後、50℃/時の降温速度で600℃まで冷却し、この温度で4時間保持した後、100℃/時の降温速度で室温まで冷却した。この焼結工程により多孔質ハイドロキシアパタイト焼結体を作製し、得られた焼結体の気孔率及び3点曲げ強度を測定した。また焼結体表面をフライスを用いて0.1 mm削り、表面を走査型電子顕微鏡で観察した。気孔率及び3点曲げ強度の測定結果を出発原料組成とともに表1に示し、走査顕微鏡写真を図1 (30倍) 及び図2 (200倍) に示す。

【0040】比較例1

ハイドロキシアパタイトの配合量を850 gとし、メチルセルロースの1重量%水溶液の配合量を1975 gとし、得られたスラリーをKENMIXミキサー（攪拌時の実際の出力：5.5 W/L、回転数150 rpm、(株)愛工舎製作所製）を用いて攪拌した以外は実施例1と同様にして注型、ゲル化、乾燥、加工及び焼結を行い、多孔質ハイドロキシアパタイト焼結体を作製した。得られた焼結体の気孔率及び3点曲げ強度を測定した。また焼結体の表面を実施例1と同様に走査型電子顕微鏡で観察した。気孔率及び3点曲げ強度の測定結果を出発原料組成とともに表1に示し、走査顕微鏡写真を図3 (30倍) 及び図4 (2000倍) に示す。3点曲げ強度はJIS R1601に準拠し、スパン1.7 cmでの測定により求めた破壊荷重から下記式：

$$\text{強度 (kgf/cm}^2\text{)} = (3 \times P \times L) / (2 \times a \times b^2)$$

P・・・破壊荷重 (kgf)

L・・・スパン (cm)

a・・・供試体 (焼結体) の高さ (cm)

b・・・供試体 (焼結体) の幅 (cm)

により算出した。

【0041】実施例2

ハイドロキシアパタイトの配合量を120 gとし、メチルセルロースの1重量%水溶液の配合量を250 gとし、得られたスラリーをPA92（攪拌時の実際の出力：60 W/L、

回転数8000 rpm、エスエムテ（株）製）により1分間攪拌した以外は実施例1と同様にして注型、ゲル化、乾燥、加工及び焼結を行い、多孔質ハイドロキシアパタイト焼結体を作製した。得られた焼結体の気孔率及び3点曲げ強度を測定した。測定結果を出発原料組成とともに表1に示す。

【0042】比較例2

スラリーの攪拌をEUROSTAR（攪拌時の実際の出力：30 W/L、回転数1000 rpm、IKA社製）により15分間攪拌した以外は実施例2と同様にして注型、ゲル化、乾燥、加工及び焼結を行い、多孔質ハイドロキシアパタイト焼結体を作製した。得られた焼結体の気孔率及び3点曲げ強度を測定した。測定結果を出発原料組成とともに表1に示す。

【0043】実施例3

攪拌装置による攪拌時間を1時間にした以外は実施例2と同じ条件でスラリーの攪拌を行った。次いで実施例2と同様にして注型、ゲル化、乾燥、加工及び焼結を行い、多孔質ハイドロキシアパタイト焼結体を作製した。得られた焼結体の気孔率及び3点曲げ強度を測定した。測定結果を出発原料組成とともに表1に示す。

【0044】比較例3

攪拌装置としてKENMIXミキサー（攪拌時の実際の出力：5.5 W/L、回転数150 rpm、(株)愛工舎製作所製）を用いた以外は実施例3と同じ条件でスラリーの攪拌を行った。次いで実施例2と同様にして注型、ゲル化、乾燥、加工及び焼結を行い、多孔質ハイドロキシアパタイト焼結体を作製した。得られた焼結体の気孔率及び3点曲げ強度を測定した。測定結果を出発原料組成とともに表1に示す。

【0045】実施例4

実施例1と同様にスラリーを作製し、これを真空オーブン中40℃、0.1 torrで脱泡させた。脱泡後のスラリーについて実施例1と同様にして注型、ゲル化、乾燥、加工及び焼結を行い、多孔質ハイドロキシアパタイト焼結体を作製した。得られた焼結体の気孔率及び3点曲げ強度を測定した。測定結果を出発原料組成とともに表1に示す。

【0046】

表1

項目	実施例1	比較例1	実施例2	比較例2
HA-11%水溶液	340 g	1975 g	250 g	250 g
HA粉体 ^(*)	150 g	850 g	120 g	120 g
攪拌装置	PA-92	KENMIX	PA92	EUROSTAR
攪拌回転数	5500 rpm	150 rpm	8000 rpm	1000 rpm
攪拌時間	15分	15分	1分	15分
攪拌装置の最大出力	120 W	650 W	120 W	75 W
	2400 W/L	329 W/L	2400 W/L	2000 W/L
実際の出力	50 W/L	5.5 W/L	60 W/L	30 W/L
気孔率	40.0 %	40.0 %	50.0 %	50.0 %

11

12

3点曲げ強度 25.0 MPa 15.0 MPa 17.0 MPa 11.0 MPa

注 * : ハイドロキシアパタイト粉体。

【0047】

表1 (続き)

項目	実施例3	比較例3	実施例4
ハイドロキシアパタイト1%水溶液	250 g	250 g	340 g
HA粉体 ^(*)	120 g	120 g	150 g
攪拌装置	PA92	KENMIX	PA92
攪拌回転数	8000 rpm	150 rpm	5500 rpm
攪拌時間	60分	60分	15分
攪拌装置の最大出力	120 W	650 W	120 W
	2400 W/L	329 W/L	2400 W/L
実際の出力	60 W/L	5.5 W/L	50 W/L
気孔率	25.0 %	25.0 %	5.0 %
3点曲げ強度	51.0 MPa	35.0 MPa	100 MPa

注 * : ハイドロキシアパタイト粉体。

【0048】表1から明らかなように、本発明の多孔質リン酸カルシウム系セラミックス焼結体は曲げ強度において優れている。また実施例1の多孔質ハイドロキシアパタイト焼結体は、比較例1のものと同程度の気孔率であるにもかかわらず、梁となるマトリックス部分が太く(図2及び図4参照)、また50～500 μ mの気孔径を有しており、比較例1のものと比べて微細な気孔が多いことが分かる(図1及び図3参照)。

【0049】

【発明の効果】以上詳述した通り、多孔質リン酸カルシウム系セラミックス焼結体を製造する本発明の方法は、仮焼処理を施したリン酸カルシウム系セラミックス粉体と水溶性高分子化合物との極めて粘調なスラリーを著しく強く攪拌するものであり、その結果マトリックス部分が太く且つその焼結性が強く、気孔サイズが揃った焼結体を得られる。本発明の方法によれば、乾燥の際の収縮がほぼ等方的に進行するため、乾燥工程で割れ等を生じることなく、適度な気孔率と高強度の多孔質リン酸カル

シウム系セラミックス焼結体を効率的に製造することができる。

【0050】本発明の多孔質リン酸カルシウム系セラミックス焼結体は5～50%の適度な気孔率だけでなく高い機械的強度及び切削性を有するので、細胞及び生体組織の培養に用いる担体や骨補填用等に好適な生体親和性を有する人工生体材料のみならず、液体クロマトグラフィー用充填剤、触媒担体、各種電気・電子材料、原子炉材料、セラミック発熱体等にも有用である。

【図面の簡単な説明】

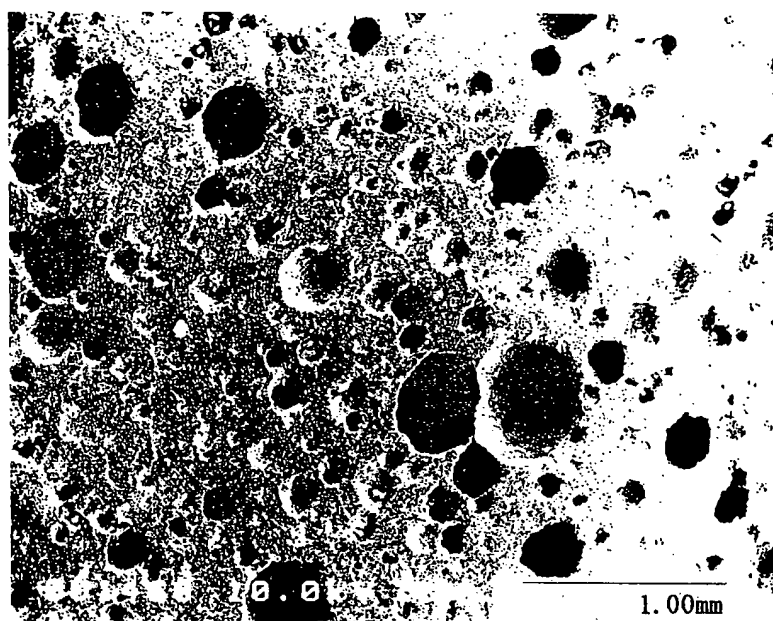
【図1】 実施例1で得られた多孔質ハイドロキシアパタイト焼結体の走査顕微鏡写真(30倍)である。

【図2】 実施例1で得られた多孔質ハイドロキシアパタイト焼結体の走査顕微鏡写真(2000倍)である。

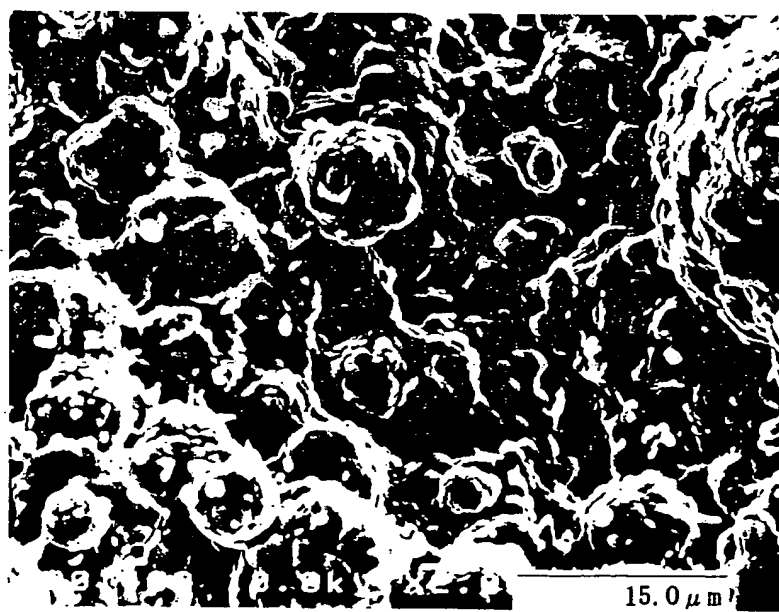
【図3】 比較例1で得られた多孔質ハイドロキシアパタイト焼結体の走査顕微鏡写真(60倍)である。

【図4】 比較例1で得られた多孔質ハイドロキシアパタイト焼結体の走査顕微鏡写真(2000倍)である。

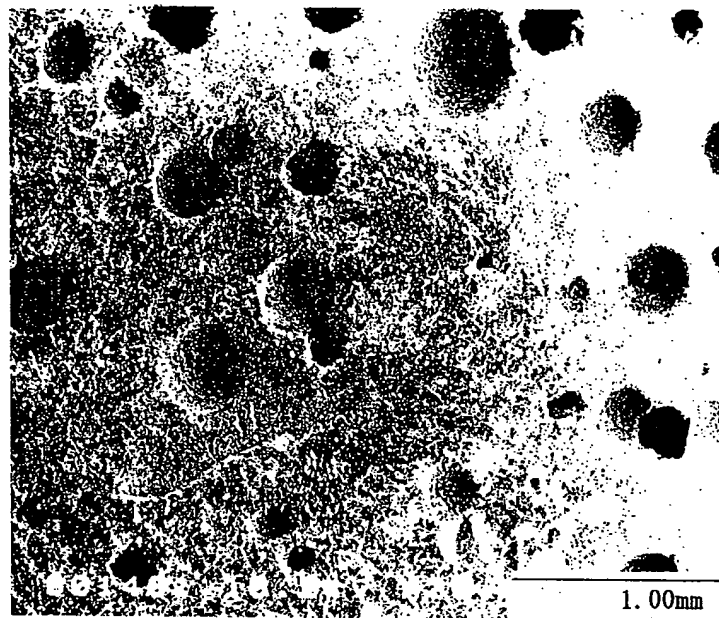
【図1】



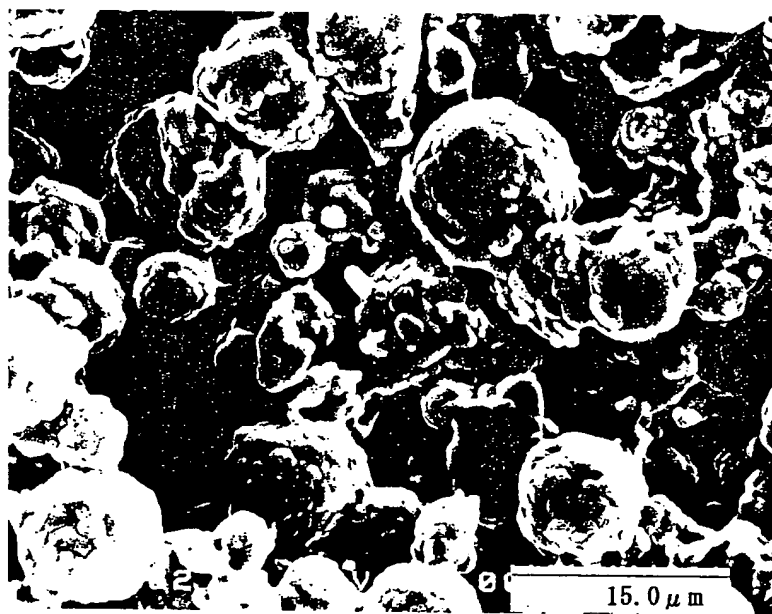
【図2】



【図3】



【図4】



PATENT ABSTRACTS OF JAPAN

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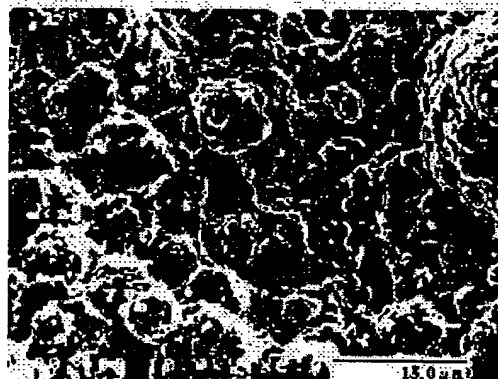
(72)Inventor : MATSUMOTO TOMOO

(54) PRODUCTION METHOD FOR CALCIUM PHOSPHATE-BASED POROUS CERAMIC SINTERED COMPACT AND CALCIUM PHOSPHATE-BASED POROUS CERAMIC SINTERED COMPACT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a production method for a calcium phosphate-based porous ceramic sintered compact having moderate porosity and high strength.

SOLUTION: This method for producing a calcium phosphate-based porous ceramic sintered compact having 5 to 50% of porosity by utilizing the gelation of a water soluble polymer comprises (1) making a slurry containing a calcined calcium phosphate-based ceramic powder and a water soluble polymer compound, (2) pulverizing and dispersing the ceramic powder in the slurry by agitating it, (3) performing a gelation, and (4) sintering after drying.



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CLAIMS

[Claim(s)]

[Claim 1] In the approach of manufacturing the porosity calcium phosphate system ceramic sintered compact whose porosity is 5 - 50% using gelation of a water soluble polymer (1) The slurry containing the calcium phosphate system ceramic fine particles which performed temporary quenching treatment, and a water soluble polymer compound is produced. (2) By stirring said slurry strongly, said calcium phosphate system ceramic fine particles are ground and distributed, and it is (3). It is made to gel and is (4). The manufacture approach of the porosity calcium phosphate system ceramic sintered compact characterized by sintering after desiccation.

[Claim 2] It is the mean particle diameter 5-20 which, as for said calcium phosphate system ceramic fine particles, average major-axis length becomes from the primary particle of the calcium phosphate system ceramics below 100 nm in the manufacture approach of a porosity calcium phosphate system ceramic sintered compact according to claim 1. The manufacture approach of the porosity calcium phosphate system ceramic sintered compact characterized by being the spherical aggregated particle of mum.

[Claim 3] the manufacture approach of a porosity calcium phosphate system ceramic sintered compact according to claim 1 or 2 — setting — the weight ratio of calcium/P of said calcium phosphate system ceramic fine particles — 1.5-1.7 it is — the manufacture approach of the porosity calcium phosphate system ceramic sintered compact characterized by things.

[Claim 4] The manufacture approach of the porosity calcium phosphate system ceramic sintered compact characterized by performing said temporary quenching treatment by 700 - 850 ** in the manufacture approach of a porosity calcium phosphate system ceramic sintered compact according to claim 1 to 3.

[Claim 5] It is the manufacture approach of the porosity calcium phosphate system ceramic sintered compact characterized by said water soluble polymer compound being a cellulosic in the manufacture approach of a porosity calcium phosphate system ceramic sintered compact according to claim 1 to 4.

[Claim 6] The manufacture approach of the porosity calcium phosphate system ceramic sintered compact characterized by stirring said slurry according to the stirring force more than 50 W/L in the manufacture approach of a porosity calcium phosphate system ceramic sintered compact according to claim 1 to 5.

[Claim 7] It sets to the manufacture approach of a porosity calcium phosphate system ceramic sintered compact according to claim 1 to 6, and they are stirring grinding and distributed processing of said slurry 1-60 The manufacture approach of the porosity calcium phosphate system ceramic sintered compact characterized by carrying out between parts.

[Claim 8] It sets to the manufacture approach of a porosity calcium phosphate system ceramic sintered compact according to claim 1 to 7, and they are said calcium phosphate system ceramic fine particles 100. It is said water soluble polymer compound 1-10 to the weight section. The manufacture approach of the porosity calcium phosphate system ceramic sintered compact characterized by blending the weight section.

[Claim 9] It is the manufacture approach of the porosity calcium phosphate system ceramic

sintered compact which sets to the manufacture approach of a porosity calcium phosphate system ceramic sintered compact according to claim 1 to 8, and is characterized by the sum density of said calcium phosphate system ceramic fine-particles + aforementioned water soluble polymer compound in said slurry being 20 – 50 % of the weight.

[Claim 10] The manufacture approach of the porosity calcium phosphate system ceramic sintered compact characterized by said calcium phosphate system ceramic fine particles being hydroxyapatite fine particles in the manufacture approach of a porosity calcium phosphate system ceramic sintered compact according to claim 1 to 9.

[Claim 11] The porosity calcium phosphate system ceramic sintered compact obtained by the manufacture approach of a porosity calcium phosphate system ceramic sintered compact according to claim 1 to 10.

[Claim 12] The porosity calcium phosphate system ceramic sintered compact characterized by having the three-point flexural strength more than 15 MPa in a porosity calcium phosphate system ceramic sintered compact according to claim 11.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention only not only in the artificial biomaterial which has the suitable biocompatibility for support, an object for bone supplementation, etc. which are used for culture of a cell and a body tissue The bulking agent for liquid chromatography, catalyst support, various kinds of electrical and electric equipment and electronic ingredients, It is related with the porosity calcium phosphate system ceramic sintered compact obtained by the method of manufacturing a useful porosity calcium phosphate system ceramic sintered compact to a nuclear reactor material, a ceramic heater, etc., and its manufacture approach. It is related with the porosity calcium phosphate system ceramic sintered compact obtained by the method of manufacturing the porosity calcium phosphate system ceramic sintered compact which has especially high intensity, and its manufacture approach.

[0002]

[Description of the Prior Art] As for the ceramics, various kinds of heat resisting materials, structure material, and functional material to which technological innovation progressed to and applied thermal resistance, a mechanical strength, insulation, a ferroelectricity, piezoelectric, semi-conductivity, magnetism, etc. are developed quickly in recent years. Especially, since the mineral constituent and structure of a gear tooth or a bone are alike, the calcium phosphate system ceramics (for example, hydroxyapatite) has the outstanding biocompatibility, and is used as biomaterials, such as a dental implant, and bone supplementation material, dental cement.

[0003] The viewpoint of biocompatibility to the calcium phosphate system ceramics is so good that porosity is so high that porosity. For this reason, the water soluble polymer gelling method is proposed as an approach of manufacturing the porosity calcium phosphate system ceramics from the former. The water soluble polymer gelling method is the approach of drying, where it made it gel by heating the slurry which was made to carry out foam formation and carried out foam formation and air bubbles are held by stirring the slurry of the ceramics and a water soluble polymer compound (JP,3058174,B). The porous ceramics obtained by the approach of JP,3058174,B are the apertures 20-2000 originating in air bubbles. It has the globular form macro pore of mum, and the three-dimension free passage hole formed of the gap of the spherical aggregated particle fine particles which consist of floc of a ceramic raw material primary particle.

[0004] However, the porosity calcium phosphate system ceramics obtained by such water soluble polymer gelling method had the weak degree of sintering of a matrix part, it is difficult to obtain a high mechanical strength, and it needs to improve mechanical strengths, such as flexural strength.

[0005] Therefore, the object of this invention is offering the manufacture approach of a porosity calcium phosphate system ceramic sintered compact of having moderate porosity and high intensity.

[0006]

[Means for Solving the Problem] In view of the above-mentioned technical problem, wholeheartedly, by stirring strongly the slurry containing the calcium phosphate system ceramic

fine particles which performed temporary quenching treatment, and a water soluble polymer compound, this invention persons discovered that the porosity calcium phosphate system ceramic sintered compact which has moderate porosity and high intensity was obtained, and completed this invention as a result of research.

[0007] Namely, the approach of this invention of manufacturing the porosity calcium phosphate system ceramic sintered compact which has porosity 5 – 50 % using gelation of a water soluble polymer (1) The slurry containing the calcium phosphate system ceramic fine particles which performed temporary quenching treatment, and a water soluble polymer compound is produced. (2) By stirring a slurry strongly, calcium phosphate system ceramic fine particles are ground and distributed, and it is (3). It is made to gel and is (4). It is characterized by sintering after desiccation.

[0008] For calcium phosphate system ceramic fine particles, the mean particle diameter which average major-axis length (the average die length of the direction of a major axis) becomes from the primary particle of the calcium phosphate system ceramics below 100 nm is 5–20. Consisting of a spherical aggregated particle of mum is desirable. It is the mean particle diameter of an aggregated particle 5–20 When it becomes a final porosity calcium phosphate system ceramic sintered compact by being referred to as mum and making the configuration spherical, and a sintered compact with the thick matrix part used as a beam is obtained and reinforcement improves, the moldability of the Green block which are the stirring nature of a slurry and the desiccation object of gel improves. the weight ratio of calcium/P of calcium phosphate system ceramic fine particles — 1.5–1.7 it is — a thing is desirable.

[0009] As for temporary quenching treatment, it is desirable to carry out at the temperature of 700 – 850 **. 700 It is –850 ** and the reinforcement of calcium phosphate system ceramic fine particles can be raised by carrying out, without being accompanied by the grain growth by sintering.

[0010] As for a water soluble polymer compound, it is desirable that they are cellulosics, such as methyl cellulose and a carboxymethyl cellulose. For the presentation of a slurry, a water soluble polymer compound is 1–10 to the calcium phosphate system ceramic fine-particles 100 weight section. It is desirable that it is the weight section. Since gelation becomes easy by this and slurry viscosity becomes moderate, grinding of an aggregated particle becomes easy. Moreover, as for the sum density of the calcium phosphate system ceramic fine-particles + water soluble polymer compound in a slurry, it is desirable that it is 20 – 50 % of the weight. Since the desiccation after gelation becomes easy by this and slurry viscosity becomes moderate, grinding of an aggregated particle becomes easy.

[0011] It is desirable that the stirring force more than 50 W/L performs, and stirring grinding and distributed processing of a slurry are 1–60. It is desirable to carry out between parts.

[0012] Especially the manufacture approach of the porosity calcium phosphate system ceramic sintered compact of this invention of having such a description is desirable when manufacturing a porosity hydroxyapatite sintered compact.

[0013] Since a matrix part is thick and the degree of sintering of the porosity calcium phosphate system ceramic sintered compact of 5 – 50 % is strong, the porosity obtained by the manufacture approach of this invention has the outstanding mechanical strength, i.e., the three-point flexural strength more than 15 MPa.

[0014]

[Embodiment of the Invention] The manufacture approach of this invention and the porosity calcium phosphate system ceramic sintered compact obtained by that cause are explained to a detail below.

[0015] [1] As calcium phosphate system ceramics used for manufacture approach this invention, although there is especially no limit, the thing of 1.5–1.7 has the desirable weight ratio of calcium/P, for example, hydroxyapatite, tricalcium phosphate, and such mixture are mentioned. The weight ratio of calcium/P is 1.7. Since it becomes a mixture phase with a calcium oxide (CaO) after super-***** and sintering, it is not desirable. Conversely, if a weight ratio becomes lower than 1.5, decomposition of the calcium phosphate itself will become easy to take place. The desirable example of the porosity calcium phosphate system ceramic sintered compact

which applies the manufacture approach of this invention is a porosity hydroxyapatite sintered compact [calcium₁₀(PO₄)₆ and 2]. Although the manufacture approach of this invention is explained to a detail taking the case of the case where a porosity hydroxyapatite sintered compact is manufactured, below, this invention is applicable to other calcium phosphate system ceramic sintered compacts.

[0016] (1) Prepare the slurry containing the preparation hydroxyapatite fine particles and the water soluble polymer compound of a slurry.

(a) It is necessary to carry out temporary quenching of the preparation hydroxyapatite fine particles of hydroxyapatite fine particles. While the reinforcement of hydroxyapatite fine particles increases, and too much grinding is not performed at the time of the below-mentioned grinding but control of a reduction ratio becomes easy by performing temporary quenching treatment, the fine-particles reinforcement which is equal to strong stirring is obtained. Hydroxyapatite fine particles are the mean particle diameter 5-20 which average major-axis length becomes from the primary particle below 100 nm. Consisting of a spherical aggregated particle of mum is desirable. When the average major-axis length of a primary particle exceeds 100 nm, when a primary particle is corned and it is made an aggregated particle, the crystal grain becomes big and rough too much, and the mean particle diameter of an aggregated particle is 5-20. In addition to what cannot be easily set to mum, sintering also becomes difficult. As for the average major-axis length of a primary particle, it is desirable that it is 5 - 80 nm. An aggregated particle corns a primary particle and makes it granularity. In order to granulate the primary particle of hydroxyapatite, the well-known corning methods, such as the spray-drying method, can be used. It is the mean particle diameter of an aggregated particle 5-20 When it becomes a final porosity hydroxyapatite sintered compact by being referred to as mum and making the configuration spherical, and a sintered compact with the thick matrix part used as a beam is obtained and reinforcement improves, the moldability of the Green block which are the stirring nature of a slurry and the desiccation object of gel improves.

[0017] Although heat-treated to an aggregated particle at a temporary-quenching-treatment process, it is desirable to process at the temperature of 700 - 850 **, and, as for the processing time, it is desirable that it is 4 - 10 hours. Sufficient improvement in the reinforcement of hydroxyapatite fine particles cannot be attained as temporary-quenching temperature is less than 700 degrees C, but since 850 ** super-***** and sintering start, grain growth takes place. More desirable temporary-quenching temperature is 700 - 750 **. A moldability and handling nature do not improve substantially that temporary-quenching time amount is less than 4 hours. Moreover, 10 If time amount is exceeded, a sintering reaction will advance and sintering after shaping will become imperfection. In addition, although temporary quenching can be performed in atmospheric air, you may carry out in inert gas in order to prevent oxidation.

[0018] (b) Gel the water soluble polymer compound which can be used for water soluble polymer compound this invention by giving means, such as heating, to the water solution or water dispersion. A water solution or a water dispersion includes both a water solution the colloidal solution an emulsion and suspension. As such a water soluble polymer compound, synthetic polymers, such as polysaccharide, such as cellulose, such as methyl cellulose and a carboxymethyl cellulose, and curdlan, polyvinyl alcohol, polyacrylic acid, polyacrylamide, and a polyvinyl pyrrolidone, etc. are mentioned, and methyl cellulose is desirable especially. Moreover, it can be made to gel by adding boric acid or borax in the case of polyvinyl alcohol.

[0019] (c) Set in a compounding ratio and a concentration slurry, and they are hydroxyapatite fine particles 100 It considers as the weight section and is a water soluble polymer compound 1-10 It is desirable to make it the weight section. Gelation is difficult in the addition of a water soluble polymer compound being under 1 weight section, and it is 10. Since the viscosity of weight ***** and a slurry becomes high too much, grinding of an aggregated particle becomes difficult. The more desirable addition of a water soluble polymer compound is 1-5. It is the weight section.

[0020] The sum density of the hydroxyapatite fine-particles + water soluble polymer compound in a slurry is 20-50. It is desirable that it is weight %. The sum density of these components is 20. The desiccation after gelation takes time amount too much as it is under weight %, and gel is

crushed after desiccation, and a porosity configuration cannot be maintained. On the other hand, sum density is 50. Since the viscosity of weight % super-***** and a slurry becomes high too much, stirring grinding of an aggregated particle is difficult. More desirable sum density is 25-40. It is weight %.

[0021] (2) If the slurry of the grinding / distribution above-mentioned presentation is stirred strongly, it can grind from a front face, the aggregated particle, i.e., the hydroxyapatite fine particles, which carried out temporary quenching. The spherical nature of a particle improves by grinding, a sintered compact with the thick matrix part used as a beam is obtained, and, as a result, the reinforcement of a sintered compact can be raised. Moreover, since the fines produced by grinding serve as a binder of aggregated particles, it contributes to the improvement in on the strength of a sintered compact. For grinding, the mean particle diameter of an aggregated particle is 5-20. It is desirable to carry out to extent which falls within the range of μm . Porosity with 5 - 50 % moderate by this, high intensity, and 5-1500 The sintered compact which has the average pore diameter of μm can be obtained. By having the porosity and average pore diameter of the above-mentioned range, when a sintered compact is used as an artificial biomaterial, the take of a cell and adsorption of various body tissues become advantageous. The mean particle diameter of an aggregated particle is 5. When handling nature does not improve that it is under μm , a particle gap becomes narrow, the consistency of a particle goes up too much, and the porosity of 5 - 50 % is not obtained. Moreover, 20 The contact range exceeding μm per grain children's unit surface area decreases in number, the bonding strength of mutual particles declines, and it becomes intolerable at the activity as bone supplementation material from a strong point.

[0022] As for the stirring force, it is desirable that it is more than 50 W/L. By carrying out stirring conditions to more than 50 W/L, an aggregated particle can be ground efficiently. Grinding is inadequate in the stirring force being under 50 W/L, and the porosity hydroxyapatite which has high reinforcement is not obtained. In addition, the stirring force can be found by
$$[\text{amount [of (the maximum output W) / water solution of an agitator] (L)]} \times (\text{actual rotational frequency / maximum engine speed})$$
. When the viscosity of a slurry becomes high, the output of an agitator increases seemingly, in order to maintain a rotational frequency. The sum density of the hydroxyapatite-case of this invention fine-particles + water soluble polymer compound in a slurry is 20-50. Since it is weight %, slurry viscosity teaches and does not change from the viscosity at the time substantially. Therefore, the effect of viscosity can be disregarded substantially.

[0023] An impeller type homogenizer is mentioned as equipment with which such stirring force is acquired. Moreover, while making an impeller into the shape of a disk, it is desirable to use the stirring equipment of the structure which prepared the irregularity on a serrated knife in the periphery of a disk, and formed the baffle in the wall of a stirring container further. The impeller type homogenizers which have such structure are PH91, PA92 and HF93 made from S EMUTE, FH94P, PD96, and HM10 grade.

[0024] Generally mixing time is 1-60, although it is dependent on the stirring force. Extent between parts is desirable. It is desirable to include air bubbles in obtaining the sintered compact of moderate porosity at the time of stirring, and it is desirable detailed and to stir air bubbles at low temperature comparatively, in order to make it stabilize, while making it equalize. Specifically, it is desirable about 0 - 25 **, and to carry out by the solution temperature of 5 - 20 ** especially. Moreover, the higher sintered compact of porosity can be obtained by pouring inert gas, such as air, nitrogen, and an argon, into the slurry under stirring.

[0025] As for the slurry ground and distributed, it is desirable to carry out casting to the mold which stretched the flexible water resisting property film to the wall. Since the film exfoliates from a mold with contraction of the ceramics at the time of desiccation by this, neither collapse of the ceramics in the field which touches a mold, nor the crack in the interior happens, but the outstanding desiccation object is acquired.

[0026] (3) In order to obtain a high sintered compact whenever precise from vacuum degassing, it is desirable to perform vacuum degassing. For example, after carrying out casting to the above-mentioned mold, degassing is put in and carried out to vacuum oven etc. Since the

porosity of a sintered compact will become low if the conditions of vacuum degassing are too severe, it is not desirable. Generally a slurry is set to 40 **, and it is 60–180 at 0.1 – 1.0 torr. If a part indirect desulfurization bubble is carried out, the sintered compact excellent in the balance of whenever [precise], and porosity will be obtained.

[0027] (4) If the slurry fully ground and distributed by gelation stirring is heated under to 100 ** more than 80 **, it will gel according to an operation of water soluble polymer compounds, such as methyl cellulose. Moisture boils that gelation is inadequate in whenever [stoving temperature] being under 80 **, and it is more than 100 **, and the gel structure is destroyed.

[0028] (5) As for desiccation of desiccation gel, it is desirable to carry out by holding to the elevated temperature (for example, under more than 80 ** – 100 **) which is extent which moisture does not boil. While contracting gel almost isotropic by desiccation, change serves as a high desiccation object (Green block) of the reinforcement which has detailed and uniform spherical macro pore at air bubbles, without producing a crack etc., since it does not happen. If moisture is lost mostly, it is good as for more than 100 **.

[0029] (6) Since the water soluble polymer compound contained in a processing Green block acts as a binder, it has the mechanical strength which can be handled. Therefore, cutting can be carried out with a desiccation object, without performing temporary baking to the Green block.

[0030] (7) In order to remove a water soluble polymer compound from the Green block which processed the cleaning predetermined configuration, perform cleaning processing if needed.

Cleaning processing can be performed by heating to 300 – 900 **.

[0031] (8) It is a sintering Green block at 1000 – 1250 ** 2–10 It sinters in time amount atmospheric air. The porosity hydroxyapatite sintered compact which has sufficient reinforcement as sintering temperature is under 1000 ** will not be obtained, and 1250 ** super-***** and hydroxyapatite will be disassembled into tricalcium phosphate and a calcium oxide. What is necessary is just to set up sintering time amount suitably according to sintering temperature. In addition, when skipping a cleaning process, it can serve as cleaning by carrying out temperature up gradually until it reaches sintering temperature. For example, it is desirable to carry out temperature up from a room temperature to about 600 ** with the programming rate of about 10–100 degrees C/o'clock, then to carry out temperature up to sintering temperature with the programming rate at the time of about 50 – 200 **/, and to hold at this temperature. After the completion of sintering is annealed.

[0032] [2] Porosity calcium phosphate system ceramic sintered compacts including the porosity hydroxyapatite sintered compact obtained by the manufacture approach of porosity calcium phosphate system ceramic sintered compact this invention are characterized by having moderate porosity and high flexural strength. (1) The porosity calcium phosphate system ceramic sintered compact of porosity this invention has the porosity of 5 – 50 %. 5 By under %, it is not enough, and since 50 % super-** and the mechanical strength are inadequate, biocompatibility is inferior to workability or handling nature.

[0033] (2) Mechanical strengths including flexural strength fall to a general flexural strength target as porosity becomes high, but since a matrix part is thick and the degree of sintering of the porosity calcium phosphate system ceramic sintered compact of this invention is strong, they have the three-point flexural strength more than 15 MPa also in porosity 50 % on him. For this reason, it excels in workability or handling nature. Three-point flexural strength can be measured according to JIS R1601.

[0034] (3) The average pore diameter of an average pore diameter porosity calcium phosphate system ceramic sintered compact is 5–1500. It is desirable that it is mum. 5 If it is under mum, trespass formation of a cell or a blood vessel will become difficult, and it is 1500. In mum **, since it becomes difficult to obtain the stable mechanical strength, the range of fluctuation of workability or handling nature becomes large too much for every product lot. For the pore diameter in a porosity calcium phosphate system ceramic sintered compact, pore [most (80% or more) since it is desirable that it is uniform] is 50–500. It is desirable that it is the path of mum within the limits.

[0035]

[Example] Although the following examples explain this invention to a detail further, this invention

is not limited to these.

[0036] an example 1 — temporary quenching of the spherical powder object (mean particle diameter: 10 μm) 160 g of the hydroxyapatite which consists of a primary particle (pitch diameter: major-axis 78 nm, minor-axis 23 nm) of a long and slender configuration was carried out into atmospheric air by 700 ** for 4 hours.

[0037] Obtained temporary-quenching fine-particles (mean diameter: 10 μm , Ca/P ratio 1.67) 150 g and 1-% of the weight water-solution 340 g of methyl cellulose (the product made from Wako Pure Chem Industry and viscosity:4000 cps measured at 20 degrees C as a water solution 2% of the weight) were blended. The obtained slurry was supplied to the homogenizer (the product made from S EMUTE, PA92). while keeping slurry temperature at 8 degrees C — a slurry — the stirring force (the actual output at the time of stirring, 5500 rpm) of 50 W/L — 15 a part — between — while stirring strongly and making it distribute, temporary-quenching fine particles were ground.

[0038] The obtained cellular content slurry is poured into a mold, and it is 2 at 83 **. Time amount heating was carried out and it was made to gel. By holding the obtained gel to 83 **, it dried thoroughly and the Green block was acquired.

[0039] After processing the Green block into the configuration of 12.0x22.0x7.0 mm, Temperature up is carried out from a room temperature to 600 ** with the programming rate at the time of 50 **/in atmospheric air. Next, temperature up was carried out to 1200 degrees C with the programming rate at the time of 100 **/, after calcinating at this temperature for 4 hours, it cooled to 600 ** at the temperature fall rate at the time of 50 **/, and after holding at this temperature for 4 hours, it cooled to the room temperature at the temperature fall rate at the time of 100 **/. The porosity hydroxyapatite sintered compact was produced according to this sintering process, and the porosity and three-point flexural strength of a sintered compact which were obtained were measured. Moreover, the sintered compact front face was deleted 0.1 mm using the milling cutter, and the front face was observed with the scanning electron microscope. The measurement result of porosity and three-point flexural strength is shown in a table 1 with a start raw material presentation, and a scan microphotography is shown in drawing 1 (30 times) and drawing 2 (2000 twice).

[0040] Except having set the loadings of example of comparison 1 hydroxyapatite to 850 g, having set the loadings of a 1-% of the weight water solution of methyl cellulose to 1975 g, and having agitated the obtained slurry using the KENMIX mixer (the actual output at the time of stirring: 5.5 W/L, rotational frequency 150 rpm, Made in the Aicohsha Factory), casting, gelation, desiccation, processing, and sintering were performed like the example 1, and the porosity hydroxyapatite sintered compact was produced. The porosity and three-point flexural strength of a sintered compact which were obtained were measured. Moreover, the front face of a sintered compact was observed with the scanning electron microscope like the example 1. The measurement result of porosity and three-point flexural strength is shown in a table 1 with a start raw material presentation, and a scan microphotography is shown in drawing 3 (30 twice) and drawing 4 (2000 twice). From the breaking load which asked for three point flexural strength by measurement in span 1.7 cm based on JIS R1601 to the following formula: It is on-the-strength (kgf/cm²) = $(3 \times P \times L) / (2 \times a \times b^2)$.

P ... Breaking load (kgf)

L ... Span (cm)

a ... Height of a test piece (sintered compact) (cm)

b ... Width of face of a test piece (sintered compact) (cm)

It was alike and computed more.

[0041] Except having set the loadings of example 2 hydroxyapatite to 120 g, having set the loadings of a 1-% of the weight water solution of methyl cellulose to 250 g, and having agitated the obtained slurry for 1 minute by PA92 (the actual output at the time of stirring: 60 W/L, rotational frequency 8000 rpm, product made from S EMUTE), casting, gelation, desiccation, processing, and sintering were performed like the example 1, and the porosity hydroxyapatite sintered compact was produced. The porosity and three-point flexural strength of a sintered compact which were obtained were measured. A measurement result is shown in a table 1 with a

start raw material presentation.

[0042] Except having stirred stirring of example of comparison 2 slurry for 15 minutes by EUROSTAR (the actual output at the time of stirring: 30 W/L, rotational frequency 1000 rpm, product made from IKA), casting, gelation, desiccation, processing, and sintering were performed like the example 2, and the porosity hydroxyapatite sintered compact was produced. The porosity and three-point flexural strength of a sintered compact which were obtained were measured. A measurement result is shown in a table 1 with a start raw material presentation.

[0043] The slurry was stirred on the same conditions as an example 2 except having carried out mixing time by example 3 churning equipment in 1 hour. Subsequently, casting, gelation, desiccation, processing, and sintering were performed like the example 2, and the porosity hydroxyapatite sintered compact was produced. The porosity and three-point flexural strength of a sintered compact which were obtained were measured. A measurement result is shown in a table 1 with a start raw material presentation.

[0044] The slurry was stirred on the same conditions as an example 3 except having used the KENMIX mixer (the actual output at the time of stirring: 5.5 W/L, rotational frequency 150 rpm, Made in the Aicohsha Factory) as example of comparison 3 churning equipment. Subsequently, casting, gelation, desiccation, processing, and sintering were performed like the example 2, and the porosity hydroxyapatite sintered compact was produced. The porosity and three-point flexural strength of a sintered compact which were obtained were measured. A measurement result is shown in a table 1 with a start raw material presentation.

[0045] The slurry was produced like example 4 example 1, and degassing of this was carried out by 40in vacuum oven **, and 0.1 torr. Casting, gelation, desiccation, processing, and sintering were performed like [slurry / after degassing] the example 1, and the porosity hydroxyapatite sintered compact was produced. The porosity and three-point flexural strength of a sintered compact which were obtained were measured. A measurement result is shown in a table 1 with a start raw material presentation.

[0046]

Table 1 Item Example 1 Example 1 of a comparison Example 2 Example of comparison 2 methyl-cellulose 1% water solution 340 g 1975 g 250 g 250 g HA fine particles (*) 150 g 850 g 120 g 120 g stirring equipment PA-92 KENMIX PA92 An EUROSTAR stirring rotational frequency 5500 rpm 150 rpm 8000 rpm 1000 rpm mixing time 15 minutes 15 minutes 1 minute The maximum output of 15-minute stirring equipment 120 W 650 W 120 W 75 W 2400 W/L 329 W/L 2400 W/L 2000 W/L — actual — an output 50 W/L 5.5 W/L 60 W/L 30 W/L porosity 40.0 % 40.0 % 50.0 % 50.0 % 3-point flexural strength 25.0 MPa 15.0 MPa 17.0 MPa 11.0 MPa notes *: Hydroxyapatite fine particles.

[0047]

Table 1 (continuation)

An item Example 3 Example 3 of a comparison Example 4 methyl-cellulose 1% water solution 250 g 250 g 340 g HA fine particles (*) 120 g 120 g 150 g Stirring equipment PA92 KENMIX PA92 Stirring rotational frequency 8000 rpm 150 rpm 5500 rpm Mixing time 60 minutes The maximum output of 60-minute stirring [15 minute] equipment 120 W 650 W 120 W 2400 W/L 329 W/L 2400 W/L A actual output 60 W/L 5.5 W/L 50 W/L Porosity 25.0 % 25.0 % 5.0 % 3-point flexural strength 51.0 MPa 35.0 MPa 100 MPa notes *: Hydroxyapatite fine particles.

[0048] The porosity calcium phosphate system ceramic sintered compact of this invention is excellent in flexural strength so that clearly from a table 1. Moreover, in spite of being porosity comparable as the thing of the example 1 of a comparison, the matrix part used as a beam is thick (refer to drawing 2 and drawing 4), and the porosity hydroxyapatite sintered compact of an example 1 is 50-500. It has the pore diameter of mum and it turns out that there is much detailed pore compared with the thing of the example 1 of a comparison (refer to drawing 1 and drawing 3).

[0049]

[Effect of the Invention] The approach of this invention of manufacturing a porosity calcium phosphate system ceramic sintered compact stirs remarkably strongly the very ***** slurry of the calcium phosphate system ceramic fine particles and the water soluble polymer compound

which performed temporary quenching treatment, as a result, a matrix part is thick, and the degree of sintering is strong, and the sintered compact to which pore size was equal is obtained as explained in full detail above. The porosity calcium phosphate system ceramic sintered compact of moderate porosity and high intensity can be manufactured efficiently, without according to the approach of this invention, producing a crack etc. at a desiccation process, since the contraction in the case of desiccation advances almost isotropic.

[0050] Since the porosity calcium phosphate system ceramic sintered compact of this invention has not only the moderate porosity of 5 – 50 % but a high mechanical strength and cutting ability, it is useful not only to the artificial biomaterial which has the suitable biocompatibility for support, an object for bone supplementation, etc. which are used for culture of a cell and a body tissue but the bulking agent for liquid chromatography, catalyst support, various electrical and electric equipment and electronic ingredients, a nuclear reactor material, a ceramic heater, etc.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the scan microphotography (30 twice) of the porosity hydroxyapatite sintered compact obtained in the example 1.

[Drawing 2] It is the scan microphotography (2000 twice) of the porosity hydroxyapatite sintered compact obtained in the example 1.

[Drawing 3] It is the scan microphotography (60 twice) of the porosity hydroxyapatite sintered compact obtained in the example 1 of a comparison.

[Drawing 4] It is the scan microphotography (2000 twice) of the porosity hydroxyapatite sintered compact obtained in the example 1 of a comparison.

[Translation done.]

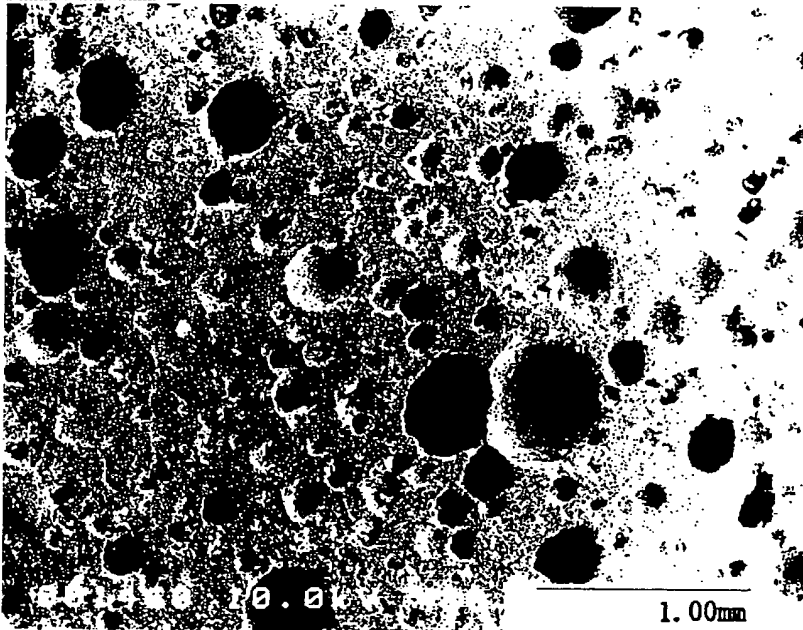
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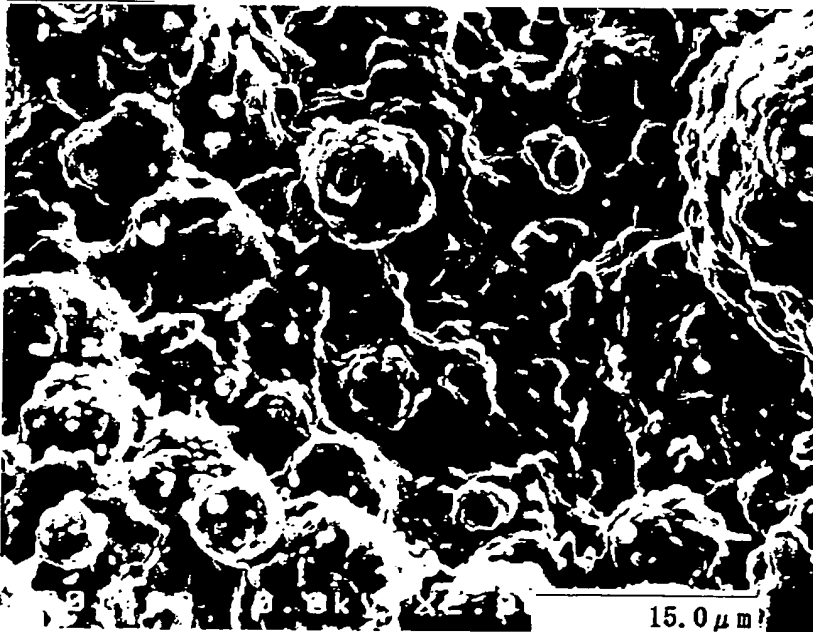
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- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS

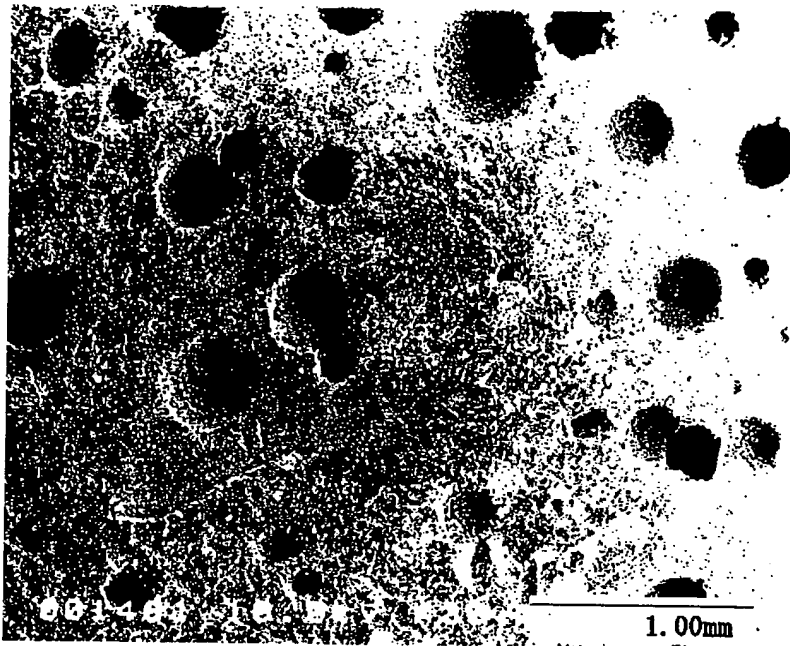
[Drawing 1]



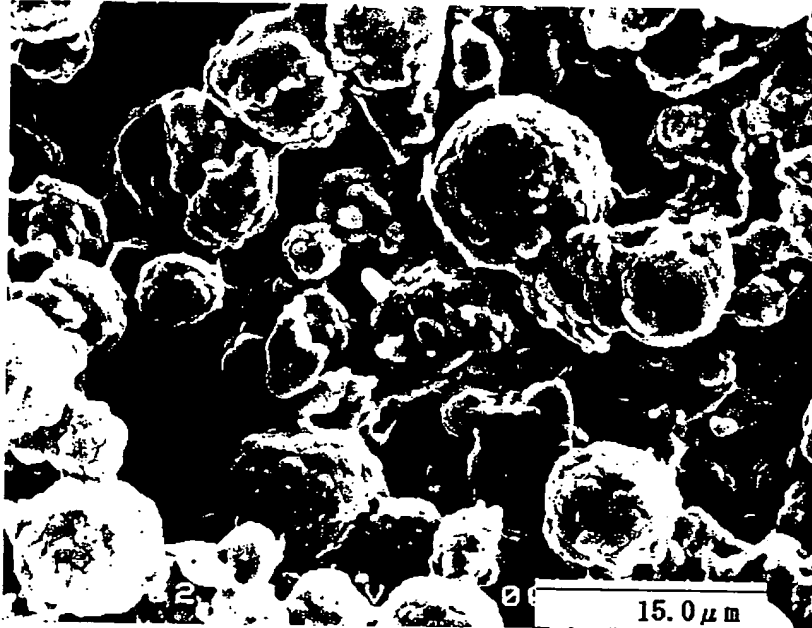
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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